

11-13-00

UTILITY PATENT APPLICATION TRANSMITTAL
(Only for new nonprovisional applications under 37 CFR 1.53(b))

11/10/00
JC921 U.S. PTO
09/710490

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09/710490

Docket No. : 41037/DBP/Y35
Inventor(s) : Kyou-Yoon Sheem, Sang-Young Yoon, Sang-Jin Kim
Title : NEGATIVE ACTIVE MATERIAL SLURRY COMPOSITION FOR RECHARGEABLE LITHIUM BATTERY AND METHOD OF MANUFACTURING NEGATIVE ELECTRODE USING SAME
Express Mail Label No. : EL483172024US

ADDRESS TO: Assistant Commissioner for Patents
Box Patent Application
Washington, D.C. 20231
Date: November 10, 2000

1. X **FEE TRANSMITTAL FORM** (*Submit an original, and a duplicate for fee processing*).

2. **IF A CONTINUING APPLICATION**

___ This application is a ___ of patent application No. .

Prior application information: Examiner ; Group Art Unit:

___ This application claims priority pursuant to 35 U.S.C. §119(e) and 37 CFR §1.78(a)(4), to provisional Application No. .

3. **APPLICATION COMPRISED OF**

Specification

15 Specification, claims and Abstract (total pages)

Drawings

1 Sheets of drawing(s) (FIGS. 1 to 1)

Declaration and Power of Attorney

___ Newly executed
X Unexecuted declaration
___ Copy from a prior application (37 CFR 1.63(d))(for continuation and divisional)

4. ___ **Microfiche Computer Program** (*Appendix*)

5. ___ **Nucleotide and/or Amino Acid Sequence Submission** (*if applicable, all necessary*)

___ Computer Readable Copy
___ Paper Copy (identical to computer copy)
___ Statement verifying identity of above copies

6. **APPLICANT(S) STATUS UNDER 37 CFR § 1.27**

___ Applicant(s) and any others associated with it/them under § 1.27(a) are a SMALL ENTITY

7. **ALSO ENCLOSED ARE**

UTILITY PATENT APPLICATION TRANSMITTAL
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Docket No.: 41037/DBP/Y35

- ☐ Preliminary Amendment
- ☐ A Petition for Extension of Time for the parent application and the required fee are enclosed as separate papers
- ☐ An Assignment of the invention with the Recordation Cover Sheet and the recordation fee are enclosed as separate papers
- ☐ This application is owned by pursuant to an Assignment recorded at Reel , Frame
- ☒ Information Disclosure Statement (IDS)/PTO-1449
- ☐ Copies of IDS Citations
- ☒ Certified copy of Priority Document(s) (*if foreign priority is claimed*)
- ☐ English Translation Document (*if applicable*)
- ☒ Return Receipt Postcard (MPEP 503) (should be specifically itemized).
- ☐ Other

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626/795-9900

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**FEE TRANSMITTAL
UTILITY PATENT APPLICATION**

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DATE: November 10, 2000

Docket No. : 41037/DBP/Y35
Inventor(s) : Kyou-Yoon Sheem, Sang-Young Yoon, Sang-Jin Kim
Title : NEGATIVE ACTIVE MATERIAL SLURRY COMPOSITION FOR
RECHARGEABLE LITHIUM BATTERY AND METHOD OF
MANUFACTURING NEGATIVE ELECTRODE USING SAME

FEE DETERMINATION

CLAIMS AS FILED					
	NUMBER FILED	NUMBER EXTRA	SMALL ENTITY RATE	LARGE ENTITY RATE	FEE
TOTAL CLAIMS	12 - 20	0	0 x \$9.00	0 x \$18.00	\$0.00
INDEPENDENT CLAIMS	2 - 3	0	0 x \$40.00	0 x \$80.00	\$0.00
MULTIPLE-DEPENDENT CLAIMS FEE			\$135.00	\$270.00	\$0.00
BASIC FEE			\$355.00	\$710.00	\$710.00
TOTAL FILING FEE					\$710.00
List Independent Claims: 1, and 7					

METHOD OF PAYMENT

☒ No filing fee enclosed
☒ No Deposit Account Authorization.

Respectfully submitted,

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**NEGATIVE ACTIVE MATERIAL SLURRY COMPOSITION FOR
RECHARGEABLE LITHIUM BATTERY AND METHOD OF
MANUFACTURING NEGATIVE ELECTRODE USING SAME**

5

CROSS REFERENCE TO RELATED APPLICATION

This application is based on application No. 99-55895 filed in the Korean Industrial Property Office on December 8, 1999, the content of which is incorporated hereinto by reference.

BACKGROUND OF THE INVENTION

(a) Field of the Invention

The present invention relates to a negative active material slurry composition for a rechargeable lithium battery and a method of manufacturing a negative electrode using the same, and more particularly, to a negative active material slurry for a rechargeable lithium slurry composition exhibiting good cycle life characteristics.

(b) Description of the Related Art

Carbonaceous material used as a negative active material for a rechargeable lithium battery are classified into amorphous carbon and crystalline graphite according to the crystallinity of the substance. Crystalline graphite includes artificial graphite and natural graphite. Typical examples of artificial graphite may include mesocarbon fiber (MCF) and mesocarbonmicro beads (MCMB). They are generally used in rechargeable lithium batteries.

The high crystallinity of natural graphite results in good initial discharge capacity, but flake type configuration materials are produced during the pulverizing step, and these flakes cause an irreversible-capacity increase at the edge of the natural graphite. In addition, natural graphite is severely compressed during electrode preparation so that it becomes difficult to absorb an electrolyte into natural graphite, and the lithium ion transferring route is longer than with artificial graphite. Accordingly, natural graphite exhibits inferior cycle life characteristics, particularly high-rate cycle life characteristics, as compared to artificial graphite of globular, fibrous or random configurations.

Japanese Patent Laid-Open No. Hei 11-40150 discloses a method producing a boron-based oxides negative electrode. The boron-based oxide negative electrode exhibits twice the cycle life characteristics of an a SnO metal oxide negative electrode. However, the boron-based oxides such as B_2O_3 are glassy and very brittle such that it is difficult to produce a negative electrode using them.

Japanese Patent No. Laid-Open No. Hei. 9-161776 discloses that metal powder such as Cu, Ni or Fe is added to an active material to increase conductivity between the active material particles, and the metal particles have a diameter one-twentieth to one-fifth that of the active material particle size. A battery using the resulting material exhibits improved cycle life characteristics. Furthermore, Japanese Patent Laid-Open No. Hei 9-245798 discloses that metal particles with a diameter of $2\ \mu m$ or less is added to an active material to increase conductivity between the active material, thereby improving cycle life

characteristics. However, conducting agents such as Cu, Ni or Fe with a one-twentieth to one-fifth diameter of the active material particles and a conducting agent with a diameter of 2 μm or less are very expensive. Furthermore, the heavy conducting agent powder tends to separate from the light active material and the conducting agent is precipitated.

Various patents such as Japanese Patent Laid-Open Nos. Hei. 8-45499 and Hei. 8-69797 disclose that copper oxide or silicate is coated on a surface of the graphite active material in the form of small islands using electroless plating to increase conductivity between the active materials. However, this method requires a high cost and additional steps for producing oxides.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a negative active material slurry composition for a rechargeable lithium battery which can improve cycle life characteristics.

It is another object to provide a method of manufacturing a negative electrode for a rechargeable lithium battery using the active material slurry composition.

These and other objects may be achieved by a negative active material slurry composition for a rechargeable lithium battery. The negative active material slurry composition includes a negative active material, a compound and an organic solvent. The compound includes elements selected from

transition metals, alkaline metals, alkaline earth metals or semi-metals.

In order to achieve these objects and others, the present invention provides a method of manufacturing a negative electrode for a rechargeable lithium battery. In this method, a negative active material is mixed with a compound that includes elements selected from transition metals, alkaline metals, alkaline earth metals or semi-metals. The mixture is added to an organic solvent to prepare a negative active material slurry composition, and the resulting product is coated on a current collector. The coated current collector is dried and the dried current collector is pressed.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the invention, and many of the attendant advantages thereof, will be readily apparent as the same becomes better understood by reference to the following detailed description when considered in conjunction with the accompanying drawings, wherein:

FIG. 1 is a graph showing cycle life characteristics of rechargeable lithium batteries used with the negative active material slurry composition of Examples of the present invention and Comparative Example.

DETAILED DESCRIPTION OF THE INVENTION

A negative active material slurry composition of the present invention includes a carbonaceous active material, a compound and an organic solvent. The compound includes elements selected from transition metals, alkaline metals, alkaline earth metals or semi-metals.

As the negative active material slurry composition of the present invention, amorphous carbonaceous material or crystalline carbonaceous materials may be used. Preferred are crystalline carbonaceous materials because they exhibit voltage flatness. The crystalline carbonaceous material includes natural graphite or artificial graphite, and preferably natural graphite exhibiting an initial discharge capacity. The natural or artificial graphite has a flake, random, disk-type, globular or fibrous configuration. The amorphous carbonaceous material may be soft carbon or hard carbon. The soft carbon is produced by heat-treating coal tar pitch, petroleum pitch, tar, or heavy oil with a low molecular weight at about 1000°C. The hard carbon is produced by heat-treating phenol resin, naphthalene resin, polyvinylalcohol resin, urethane resin, polyimide resin, furan resin, cellulose resin, epoxy resin or polystyrene resin at about 1000°C.

Generally, natural graphite has high crystallinity so that it exhibits good initial discharge capacity. But natural graphite develops a flake configuration when pulverized due to its high crystallinity, and natural graphite having a flake configuration causes increases in the irreversible capacity at its edge. In addition, natural graphite is severely compressed during electrode preparation so that it becomes difficult to absorb an electrolyte into it, and the lithium ion transferring route is longer than with artificial graphite. Accordingly, natural graphite exhibits inferior cycle life characteristics, particularly high-rate cycle life characteristics, as compared to artificial graphite with globular, fibrous or random configurations. Due to the above problems, it is difficult to use natural

graphite for the negative active material of a rechargeable lithium battery.

In the present invention, a compound including elements such as transition metals, alkaline metals, alkaline earth metals or semi-metals is added to the negative active material slurry composition so that the active material has no edge portion and is not severely compressed. As a result, natural graphite can be used for a rechargeable lithium battery without the above problems.

The organic solvent may be any solvent used in the negative active material slurry composition and the exemplary thereof may be N-methyl pyrrolidone.

The negative active material slurry composition may further include a binder for increasing adhesion between negative active material particles, and between the negative active material and the current collector. The binder is not limited to and may be polyvinylidene fluoride or water-solubility styrene-butadiene rubber. The negative active material slurry composition includes 5 to 10 wt% of the binder.

The negative active material slurry composition of the present invention is produced by mixing a negative active material, a compound, and an organic solvent. The compound includes transition metals, alkaline metals, alkaline earth metals, or semi-metals, and a binder may be added to the mixture. The negative active material slurry composition is coated (cast) on a current collector, which may be but is not limited to copper, to produce a negative electrode. The coated current collector is dried and pressed.

The negative active material slurry composition includes a compound of

transition metals, alkaline metals, alkaline earth metals, or semi-metals so that severe compression of the active material may be prevented. Accordingly, the problems due to severe compression, which are electrolyte absorbing difficulty and a long lithium ion transferring route, can be prevented.

5 Using the negative electrode, a positive electrode and non-aqueous electrolyte, a rechargeable lithium battery is manufactured by the conventional process. The positive electrode is produced by the conventional process known in the related arts, for example by coating a positive active material slurry composition on a current collector and drying. The positive active material slurry composition includes a positive active material, a binder such as polyvinylidene fluoride, and a conductive agent such as carbon black. The current collector may be Al-foil. The positive active material may be any compound used in the rechargeable lithium battery and the exemplary thereof may be transition metal oxides such as LiCoO_2 , LiNiO_2 , $\text{LiNi}_x\text{Co}_{1-x}\text{M}_y\text{O}_2$ ($0.1 < x < 1.0$, $0 \leq y \leq 1.0$, M is transition metal), LiMnO_2 or LiMn_2O_4 .

15 The electrolyte includes organic solvents and lithium salts dissolved in the organic solvent. The organic solvents may be a cyclic carbonate such as ethylene carbonate or methylene carbonate, or a linear carbonate such as dimethyl carbonate, diethyl carbonate, ethylmethyl carbonate or methylpropyl carbonate. The lithium salts may be any lithium salts with the capability of accelerating lithium ion movement between the positive and negative electrodes. The exemplary of lithium salts may be LiPF_6 , LiAsF_6 , LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_3$, LiBF_6 or LiClO_4 .

as in Example 1 except that 3 wt% of nickel hydroxide was added to the natural graphite negative active material and 5 wt% of a water-soluble styrene-butadiene rubber binder was used.

Example 3

5 A coin-type lithium half cell was manufactured by the same procedure as in Example 1 except that 3 wt% of B_2O_3 was added to the natural graphite negative active material and 5 wt% of a water-soluble styrene-butadiene rubber binder was used.

Example 4

A coin-type lithium half cell was manufactured by the same procedure as in Example 1 except that 3 wt% of calcium oxalate monohydrate was added to the natural graphite negative active material and 5 wt% of a water-soluble styrene-butadiene rubber binder was used.

Example 5

15 A coin-type lithium half cell was manufactured by the same procedure as in Example 1 except that 3 wt% of tetraethylene ortho silicate was added to the natural graphite negative active material.

Comparative Example 1

20 A coin-type lithium half cell was manufactured by the same procedure as in Example 1 except that B_2O_3 was not added to the natural graphite negative active material.

Each of the coin-type lithium half cells of Examples 1 to 5 and Comparative Example 1 was charged and discharged fifty times and then the

cycle life was measured. The results are shown in Fig. 1. As shown in Fig. 1, the half cells of Examples 1 to 3 using natural graphite with a flake configuration and a boron compound exhibits better cycle life characteristics than that of Comparative Example 1. Particularly, the cell of Example 2 using the negative active material slurry including the nickel compound exhibits superior cycle life characteristics. Furthermore, the cells of Examples 4 and 5 using an alcohol solution of metal exhibits improved cycle life characteristics by making the solution uniformly distribute the electrolyte on the surface of the active material and between particles thereof.

As described above, the negative active material slurry composition for a rechargeable lithium battery of the present invention exhibits good cycle life characteristics owing to cycle life improved material.

While the present invention has been described in detail with reference to the preferred embodiments, those skilled in the art will appreciate that various modifications and substitutions can be made thereto without departing from the spirit and scope of the present invention as set forth in the appended claims.

WHAT IS CLAIMED IS:

1. A negative active material slurry composition for a rechargeable lithium battery comprising:

a negative active material;

5 a compound comprising elements selected from the group consisting of transition metals, alkaline metals, alkaline earth metals and semi-metals; and

an organic solvent.

2. The negative active material slurry composition of claim 1 wherein the transition metal is selected from the group consisting of Mn, Ni, Fe, Cr, Co, Cu and Mo, the alkaline metal is selected from the group consisting of Na and K, the alkaline earth metal is selected from the group consisting of Ca and Mg, and the semi-metal is selected from the group consisting of B, Al, Ga, Si and Sn.

3. The negative active material slurry composition of claim 1 wherein the transition metal compound is nickel hydroxide, the alkali earth metal compound is calcium oxalate monohydrate, and the semi-metal compound is boron compounds or tetraethylene orthosilicate.

4. The negative active material slurry composition of claim 1 wherein the compound includes at least one boron compound.

20 5. The negative active material slurry composition of claim 4 wherein the boron compound includes B_2O_3 , H_2BO_3 or BF_3

6. The negative active material slurry composition of claim 1 wherein the amount of the compound is 0.05 to 30 wt %.

7. A method of manufacturing a negative electrode for a rechargeable lithium battery comprising the steps of:

mixing a negative active material with a compound, the compound comprising elements selected from the group consisting of transition metals, alkaline metals, alkaline earth metals and semi-metals;

adding an organic solvent to the mixture;

coating the resulting mixture on a current collector; and

drying the coated current collector and pressing the dried current collector.

8. The method of claim 7 wherein the transition metal is selected from the group consisting of Mn, Ni, Fe, Cr, Co, Cu and Mo, the alkaline metal is selected from the group consisting of Na and K, the alkaline earth metal is selected from the group consisting of Ca and Mg, and the semi-metal is selected from the group consisting of B, Al, Ga, Si and Sn.

9. The method of claim 7 wherein the transition metal compound is nickel hydroxide, the alkali earth metal compound is calcium oxalate monohydrate, and the semi-metal compound is boron compounds or tetraethylene orthosilicate.

10. The method of claim 7 wherein the compound includes at least one boron compound.

11. The method of claim 10 wherein the boron compound includes B_2O_3 , H_2BO_3 or BF_3

12. The method of claim 7 wherein the amount of the compound is

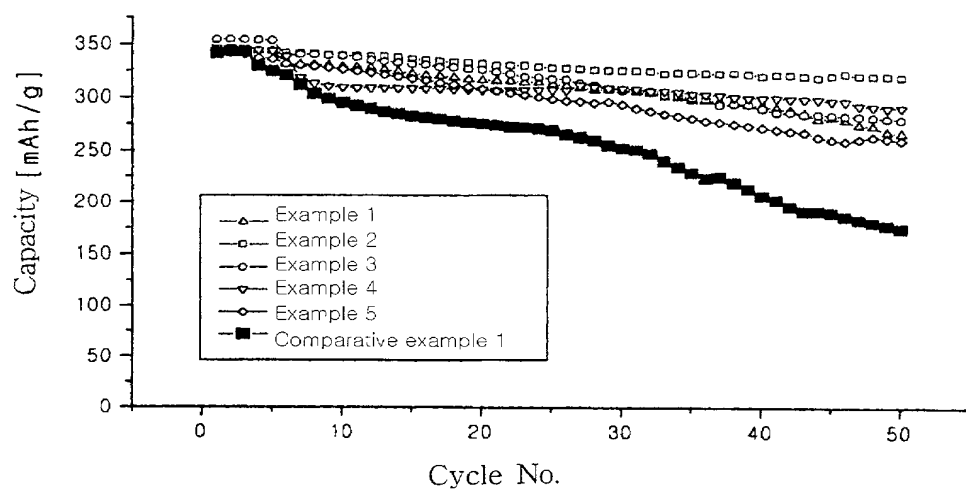
0.05 to 30 wt %.

0.05 to 30 wt %

ABSTRACT OF THE DISCLOSURE

Disclosed is a negative active material slurry composition for a rechargeable lithium battery. The negative active material slurry composition includes a negative active material, a compound and an organic solvent. The compound includes transition metals, alkaline metals, alkaline earth metals and semi-metals. The negative active material slurry composition has long cycle life owing to the compound.

FIG. 1



**DECLARATION AND POWER OF ATTORNEY
FOR PATENT APPLICATIONS**

PATENT

Docket No. : 41037/DBP/Y35

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled **NEGATIVE ACTIVE MATERIAL SLURRY COMPOSITION FOR RECHARGEABLE LITHIUM BATTERY AND METHOD OF MANUFACTURING NEGATIVE ELECTRODE USING SAME**, the specification of which is attached hereto unless the following is checked:

— was filed on _____ as United States Application Number or PCT International Application Number _____ and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of the foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)

<u>Application Number</u>	<u>Country</u>	<u>Filing Date (day/month/year)</u>	<u>Priority Claimed</u>
99-55895	Korea	8 December 1999	YES

I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below.

<u>Application Number</u>	<u>Filing Date</u>
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I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

<u>Application Number</u>	<u>Filing Date</u>	<u>Patented/Pending/Abandoned</u>
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POWER OF ATTORNEY: I hereby appoint the following attorneys and agents of the law firm CHRISTIE, PARKER & HALE, LLP to prosecute this application and any international application under the Patent Cooperation Treaty based on it and to transact all business in the U.S. Patent and Trademark Office connected with either of them in accordance with instructions from the assignee of the entire interest in this application;

**DECLARATION AND POWER OF ATTORNEY
FOR PATENT APPLICATIONS**

Docket No. 41037/DBP/Y35

or from the first or sole inventor named below in the event the application is not assigned; or from YOU ME PATENT & LAW FIRM in the event the power granted herein is for an application filed on behalf of a foreign attorney or agent.

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The authority under this Power of Attorney of each person named above shall automatically terminate and be revoked upon such person ceasing to be a member or associate of or of counsel to that law firm.

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I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Full name of second joint inventor Sang-Young Yoon	Inventor's signature	Date
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**DECLARATION AND POWER OF ATTORNEY
FOR PATENT APPLICATIONS**

Docket No. 41037/DBP/Y35

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